Structure and Intramolecular Proton Transfer of Alanine Radical Cations

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The structures of the four lowest alanine conformers, along with their radical cations and the effect of ionization on the intramolecular proton transfer process, are studied using the density functional theory and MP2 method. The energy order of the radical cations of alanine differs from that of the corresponding neutral conformers due to changes in the basicity of the NH_2 group upon ionization. Ionization favors the intramolecular proton transfer process, leading to a proton-transferred radical-cation structure, $[NH_3^+\text{-}CHCH_3\text{-}COO\bullet]$, which contrasts with the fact that a proton-transferred zwitterionic conformer is not stable for a neutral alanine in the gas phase. The energy barrier during the proton transfer process is calculated to be about 6 kcal/mol.

Key Words : Alanine radical cation, Intramolecular proton transfer, Hydrogen bond, Energy barrier, Spin density

Introduction

Hydrogen bonds that form in amino acids are of great importance in determining the three-dimensional structure of proteins. In particular, an intramolecular proton transfer is one of the most important reactions in biological chemistry and is related to the zwitterionic and neutral structures of amino acids. Alanine is the most abundant and important amino acid found in proteins, and it can be found both inside proteins in contact with water and on their surface.[1]

The structure of alanine has been studied both experimentally and theoretically by many researchers.[2-8] The first experimental studies of alanine in the solid state[9] revealed the existance of a zwitterionic form based on a small difference between the two carbon-oxygen distances and the positions of three hydrogen atoms in the ammonium ion group. Using a high pressure mass spectrometer (HPMS) and *ab initio* calculations, Wu *et al.*[10] showed that certain organic ammonium ions are able to stabilize the zwitterionic structure of amino acids. However, it was determined through electron diffraction[3] and millimeter-wave spectroscopic studies[4] that only a neutral form exists in the gas phase. Up to thirteen possible conformers were predicted for alanine through computational studies.[4,6,7]

Amino acid radicals are of significant biological importance. The effects of oxidative damage to amino acids, which plays a role in numerous pathological disorders,[11] have attracted significant interest. Oxidation can be initiated by oxidizing agents such as OH• or other radicals,[12-15] or through ionized radiation.[16] Recent studies have shown that radical cations of certain amino acids can be formed through the collision-induced dissociation of $[Cu^{II}(dien)M]\bullet^{2+}$ complex ions.[17] For this reason, the properties of different radicals derived from amino acid have attracted considerable attention during the past few years. In addition, proton transfer reactions in hydrogen-bonded systems have been widely studied both experimentally and theoretically due to their great importance

in biochemistry.[18] However, the study on the radical cations of amino acids is surprisingly small, and to the best of the author's knowledge, no computational studies have been performed on the proton transfer process in alanine radical cations.

In continuing our studies[19,20] on the organic radicals, in this paper we report the ionization process of the lowest four conformers of alanine and the intramolecular proton transfer process for the radical cation of the second-most stable alanine conformer.

Computational Details

It is well known that alanine can exist in a number of conformers due to the existence of many single-bond rotamers.[21] All theoretical calculations on the conformers considered in this study were carried out with the Gaussian 03 series of program[22] using 6-311++G(d,p).

DFT calculations were evaluated at the B3LYP level,[23] and *ab initio* calculations were performed using the MP2 level of theory. The B3LYP method has been shown to perform much better than the more computationally demanding MP2 one for different radical cations.[24] In this study, to confirm the density functional results, we have optimized some of the systems at the MP2 level. To determine the adequacy of the methods used for studying the conformational behavior of alanine, in this paper the optimized geometry is compared with recent experimental results[25] for the two most stable conformers of a neutral alanine. It has been shown that the B3LYP method provides very similar structural parameters compared with MP2 for glycine and other amino acids.[26]

The equilibrium geometries of each of the structures were fully optimized without any restriction on symmetries. All energy values of the optimized structures reported in this paper include a zero point vibrational energy correction. The vibration frequencies were also calculated to confirm whether

all the stationary points correspond to the true minima or the transition state (TS) on the potential energy surface. The stationary structures were obtained by verifying whether the harmonic frequencies all have real numbers for the local minimum, or whether one imaginary number exists for the TS. To identify the minima connected by a given transition state, intrinsic reaction coordinate (IRC) calculations were carried out at the same level of theory. Natural population analyses[27] were also performed to estimate the net atomic charges and spin densities along the pathway of the proton transfer process.

Results and Discussion

Neutral Alanine. The equilibrium geometries of the ten most stable structures of alanine were taken from a previous study[28] as the starting points for the structural optimization. The optimized geometries of the four lowest conformers of neutral alanine at the B3LYP and MP2 levels of theory are presented in Figure 1.

The two lowest conformers of neutral alanine correspond to structures I and II in Figure 1. The optimized geometry parameters at the B3LYP and MP2 levels of theory are summarized in Table 1 for the two most stable structures, I and II. The experimental data are also included. As shown in Table 1, the structural results are in good agreement with the geometry parameters derived from electron-diffraction experiments.[25]

In Figure 1, structures I and III form bifurcating hydrogen bonds between the amino group and carbonylic or hydroxylic oxygen, respectively. The second-most stable conformer in terms of energy, structure II in Figure 1, lies 0.34 kcal/mol above structure 1 at the B3LYP level. This conformer has the hydroxylic group acting as a proton donor and the amino group acting as a proton acceptor. Distance of intramolecular
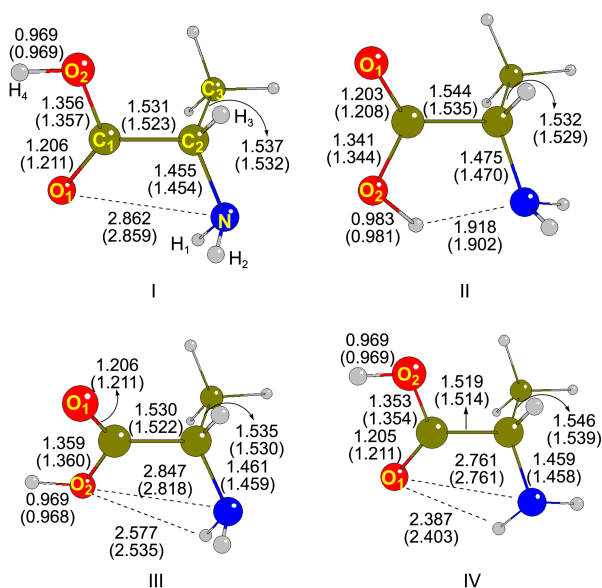
Table 1. Optimized geometrical parameters of the two most stable structures at the two levels of theory. The distances are in Å and the bond angles are in degrees
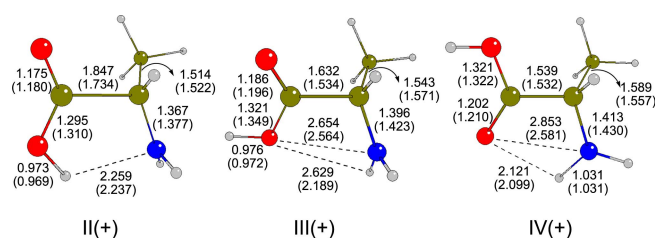
Parameters	Structure I			Structure II		
	DFT	MP2	Exp[a]	DFT	MP2	Exp[a]
$r(C_1-C_2)$	1.531	1.523	1.51(1)	1.544	1.535	1.524(7)
$r(C_2-C_3)$	1.537	1.532	1.53(2)	1.532	1.529	1.543(8)
$r(N-C_2)$	1.455	1.454	1.45(1)	1.475	1.470	1.458(9)
$r(C_1=O_1)$	1.206	1.211	1.24(2)	1.203	1.208	1.20(2)
$r(C_1-O_2)$	1.356	1.357	1.33(2)	1.341	1.344	1.37(2)
$r(N-H_4)$	4.366	4.345	4.34(2)	1.918	1.902	1.96(1)
$r(O_1-H_1)$	2.688	2.684	2.70(2)	4.380	4.384	4.31(2)
$r(O_1-H_2)$	2.934	2.894	2.88(2)	4.039	3.970	3.97(2)
$\angle(C_1C_2C_3)$	109.3	108.4	108.3(6)	109.1	108.1	107.1(3)
$\angle(C_1C_2N)$	113.6	113.7	115(1)	109.6	109.4	111.7(7)
$\angle(C_2C_1O_1)$	125.6	115.4	125(2)	122.6	122.6	125(1)
$\angle(C_2C_1O_2)$	118.8	111.4	113(2)	114.2	114.0	113(1)
$\angle(NC_2C_1C_3)$	-123.5	-122.1	-123.5(7)	-121.9	-118.9	-121.1(7)
$\angle(H_3C_2C_1C_3)$	117.0	117.5	135	117.0	117.5	118
$\angle(H_1NC_2C_1)$	-61.1	-58.0	-61(1)	-96.0	-91.6	-99.2(4)
$\angle(H_2NC_2C_1)$	56.5	58.1	60.7(7)	142.4	148.7	148
$\angle(NC_2C_1O_1)$	-18.6	-20.2	-14(1)	167.8	164.5	167(1)
$\angle(NC_2C_1O_2)$	162.1	161.4	167(1)	-13.5	-18.2	-11.5(8)
$\angle(H_4O_2C_1O_1)$	-1.1	-1.5	-1(2)	-178.5	-177.6	-179(2)

[a]From Ref. 25.

hydrogen bond between them is calculated to be 1.918 Å at B3LYP level (1.902 Å at MP2 level). Calculation of the dihedral angle (NCC=O) in conformer I showed a negative value (−18.6° at the B3LYP level), which is in agreement with previous experimental results obtained from the gas-phase electron diffraction (GED) data[3] and millimeter-wave (MMW) spectroscopy,[4] and agrees with the results from the solid state.[9(d)] Calculation of the dihedral angle (NCC-O(H)) of conformer II also showed a negative value (−13.5° at the B3LYP level). These results are due to a reduction in the repulsion between the methyl and hydroxyl groups in conformer I or between the methyl group and the

Table 2. Absolute (in a.u.) and relative energies (in kcal/mol) of the four most stable structures of neutral alanine and the corresponding ionized alanine at the two levels with 6-311++G(d,p) used as the basis set

Structure	DFT/B3LYP	*Ab initio*/MP2
Neutral, [NH$_2$-CHCH$_3$-COOH]		
I	-323.748487(0.0)	-322.879684(0.0)
II	-323.747940(0.34)	-322.878815(0.55)
III	-323.746686(1.13)	-322.878037(1.03)
IV	-323.746487(1.26)	-322.877820(1.17)
Radical Cation, [•NH$_2$-CHCH$_3$-COOH]$^+$		
II(+)	-323.414558(4.79)	-322.532029(11.12)
III(+)	-323.426244(-2.54)	-322.545420(2.72)
IV(+)	-323.422198(0.0)	-322.549755(0.0)

Figure 1. B3LYP optimized geometries of the four lowest conformers of neutral alanine. The distances are in Å and the values in parentheses are at the MP2 level.

Figure 2. B3LYP optimized geometries of the three lowest conformers of an alanine radical cation. The distances are in Å and the values in parentheses are at the MP2 level.

carbonyl oxygen in conformer II.

The absolute and relative energies of the four structures shown in Figure 1 are listed in Table 2.

As shown in Table 2, structure I is the global minimum conformer of the potential energy, and structure II was found to be the second-most stable conformer. These results are in agreement with the results from the MMW spectroscopy[4] and GED data.[3] However, conformers I and II are in a nearly degenerate state. If the zero point corrections are not taken into account, the energy difference between the two conformers is only 0.03 kcal/mol. It is notable that the MP2 results also show conformer I as being the most stable structure. The near degeneracy of these two conformers has been previously reported in different studies.[6,28,29] Recently, Blanco *et al.*[25] reported experimental results showing that conformer I is the most stable structure for alanine.

Alanine Radical Cation. Figure 2 shows the optimized geometry of radical cations derived from the ionization of the four neutral conformers considered in this study. It is noteworthy that only three stable structures were obtained upon ionization of structures I-IV shown in Figure 1.

In this study, the radical cation corresponding to structure I in Figure 1 has not been found to be a minimum on the potential energy surface. The optimization of ionized I leads to structure IV(+) at both the B3LYP and MP2 levels. This trend is similar to other reported glycine radical cations.[26]

The C-N distance decreases, whereas the C-C(CH$_3$) distance increases, upon ionization in structures II, III, and IV. On the other hand, NH$_2$ of conformer II obtains an NH$_2^+$ character upon the removal of one electron. Accordingly, the ionization of conformer II decreases the basicity of the amino group, and the intermolecular hydrogen bond is weakened. Thus, radical cation conformer II(+) presents a longer H$_2$N···H hydrogen bond (2.259 Å) than in neutral conformer II (1.918 Å). However, ionization of conformer IV increases the acidity of the amino group, and the hydrogen bond is strengthened. Accordingly, the NH···O distance decreases from 2.387 Å (IV) to 2.121 Å (IV(+)).

The calculated energies of the alanine radical cations are listed in Table 2. As can be seen in the table, conformer III(+) was found to be the most stable radical cation at the B3LYP level. It is noteworthy that at the MP2 level, conformer IV(+) was found to be the lowest in terms of energy. This inconsistency can be explained by the fact that structure III(+) presents a two-center three-electron bond between the
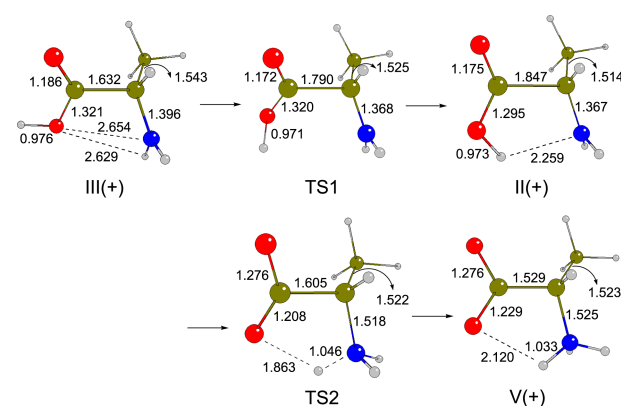
NH$_2$ and OH groups. These structures are found to be overstabilized by the DFT methods due to an overestimation of the self interaction of the exchange energy.[30] The highest radical cation conformer in terms of energy is structure II(+) at both the B3LYP and MP2 levels, which is in contrast with the neutral species. This tendency is also similar to the results found in glycine radical cations.[26] As mentioned earlier, the fact that conformer II(+) is less stable than IV(+) can be explained as follows: As the amino group is acting as a proton acceptor for conformer II(+), the ionization decreases the nitrogen basicity, and the hydrogen bond is weakend. However, since the amino group is acting as a proton donor for conformer IV(+), the hydrogen bond is strengthened due to an increase in the nitrogen acidity. Although conformer II(+) has the highest structure, this structure is the one involved in the intramolecular proton transfer process of interest.

Intramolecular Proton-transfer Process. The optimized structures of the ionized species involved in the proton transfer process of alanine radical cations are shown in Figure 3 along with the relevant TS structures. Two conformers of the alanine radical cations, II(+) and III(+), and the proton-transferred form, V(+), have been taken into account in this study following their ability to transfer protons.

Two transition state structures were found to occur during the proton transfer process. As shown in Figure 3, TS1 links the III(+) and II(+) structures, and TS2 links the II(+) and V(+) structures. As indicated by several researchers, the proton-transferred form (zwitterion) of an alanine molecule

Figure 3. B3LYP/6-311++G(d,p) optimized geometries of ionized alanines involved in the proton transfer process. The distances are in Å.

Table 3. Energies of structures II(+), III(+), V(+) and TSs involved in the proton transfer process at the B3LYP level

Structure	Total Energy (a.u.)	Rel. Energy (kcal/mol)
III(+)	-323.426244	0.0
TS1	-323.406093	12.64
II(+)	-323.414558	7.33
TS2	-323.404663	13.54
V(+)	-323.404944	13.37
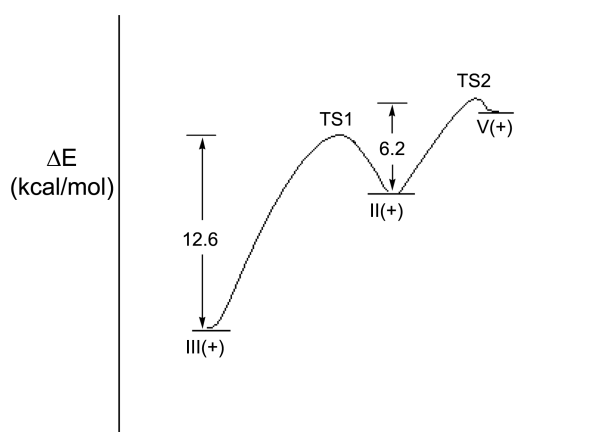
Figure 4. Reaction coordinate involved in the proton-transfer process calculated at the B3LYP level.

Table 4. Natural charge and spin density of the reactant (II(+)) and product (V(+)) involved in the proton transfer process at the B3LYP level

	Structure II(+)		Structure V(+)	
	Charge	Spin den.	Charge	Spin den.
[COOH]			[COO]	
C_1	0.84	0.12	0.72	-0.06
O_1	-0.33	0.33	-0.18	0.79
O_2	-0.58	0.06	-0.47	0.26
H	0.51	0.0		
Sum	0.44	0.51	0.06	0.99
[NH$_2$]			[NH$_3$]	
N	-0.66	0.34	-0.69	0.0
H	0.42	-0.01	0.44	0.0
H	0.42	-0.01	0.46	0.0
H			0.45	0.0
Sum	0.19	0.33	0.67	0.0

does not exist in the gas phase as intermolecular interactons have no effect in this state. However, for alanine radical cations, the proton-transferred structure [NH$_3^+$-CHCH$_3$-COO•], V(+), has been located in this study. The total and relative energies of the stationary points at the B3LYP level of theory are given in Table 3. In addition, the reaction coordinate involved in the proton-transfer process calculated at the B3LYP level of theory is shown in Figure 4.

The energy barrier for the III(+) → II(+) interconversion is calculated to be about 12.6 kcal/mol at the B3LYP level. For the process goes to V(+) from II(+) conformer, the barrier is found to be 6.2 kcal/mol. The energy barrier for the III(+) → II(+) interconversion process is larger than that of the intramolecular proton-transfer process. This means that the energy barrier of the two-step process, III(+) → II(+) → V(+), depends mainly on the conformational changes.

As shown in Figures 1 and 3, the ionization of conformer II significantly increases the C-C bond distance. As mentioned previously, ionization also decreases the nitrogen basicity, and the hydrogen bond becomes less favorable, producing an important increase in the hydrogen bond distance (from 1.918 to 2.259 Å at the B3LYP level). After the hydrogen is transfered to a nitrogen atom, structure V(+) in Figure 3, the hydrogen bond distance decreases. These results are explained in terms of the change of spin density of the N and O$_1$ atoms. To illustrate the nature of a hydrogen transfer in an alanine radical cation, the natural charges and spin densities of the reactant (II(+)) and product (V(+)) involved in the proton transfer process are summarized in Table 4.

As shown in Table 4, the spin density of structure II(+) is 0.34 for N, and 0.33 for O$_1$. After the hydrogen is transferred to a nitrogen atom, structure V(+) in Figure 3, the hydrogen bond distance decreases (from 2.259 to 2.120 Å), and consequently, the the hydrogen bond is strengthened. After a proton transfer, the spin density of the N atom is changed from 0.34 to 0.0, while the spin density of the O$_1$ atom is changed from 0.33 to 0.79. That is, the radical character in structure V(+) is nearly transferred to O$_1$. This allows O$_2$ to participate in the hydrogen bond with two electrons. There-

fore, the hydrogen bond becomes more suitable, and the hydrogen bond length is shortened. It can be observed in Table 3 that the energy barrier of the hydrogen transfer process (II(+) → V(+)) is appreciable, and the reaction is endothermic.

Conclusions

The structure of neutral alanines along with their radical cations were studied at the B3LYP and MP2 levels of theory using 6-311++G(d,p) as the basis set. Ionization of the four lowest conformers of neutral alanine, I ~ IV, leads to three stable ionic structures, II(+) ~ IV(+). The optimized geomerical parameters obtained using the DFT and MP2 levels are similar. Ionization of I leads to structure IV(+). The energy order of the ionized species differs from that observed for the neutral species. In particular, structure IV(+) becomes more stable than structure II(+). This is due to the fact that the intramolecular hydrogen bond strengthens upon ionization when the amino group acts a proton donor, IV(+), whereas the bond is weakened when acting as a proton acceptor, II(+). The zwitterionic conformer of alanine [NH$_3^+$-CHCH$_3$-COO$^-$] does not exist in the gas phase. However, ionized structure of II(+) favors the proton transfer process. For a ground ionic state, both reactant (II(+)) and product (V(+)) have similar energies. This is in contrast to what was observed for neutral alanine, of which a proton transferred (zwitterionic) conformer is not stable in the gas phase. This leads to the proton transferred conformer, [NH$_3^+$-CHCH$_3$-COO•], V(+), for an alanine radical cation. Two transition state structures have been found to occur during the conformational process. The first is a conformational interconversion, and the other a proton transfer process. The energy barrier found for the proton transfer process is smaller than the other conformational barrier. This indicates that the proton transfer process is fast compared with the structural changes. That is, in this work, the reactant (II(+)), product (V(+)), and transition state were localized during the proton

transfer process, with an energy barrier of about 6 kcal/mol at the B3LYP level.

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